THE ROYAL SOCIETY

From ferromagnets to high-spin molecules: the role of the organic ligands

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The nature of the organic ligands is crucial in influencing the dimensionality of bimetallic cyanide-bridged systems. By controlling the number of coordination sites around a metal ion, we show that systems with new structure and original architecture may be obtained. Blocking four of the coordination sites around Ni^{II} and Mn^{II}, new structures with new architectures can be obtained depending on the position of the remaining two available sites: in the *trans* or *cis* position.

Keywords: molecular magnetism; ferromagnet; metamagnet; high-spin molecules; cyanide-bridged systems; low-dimensional systems

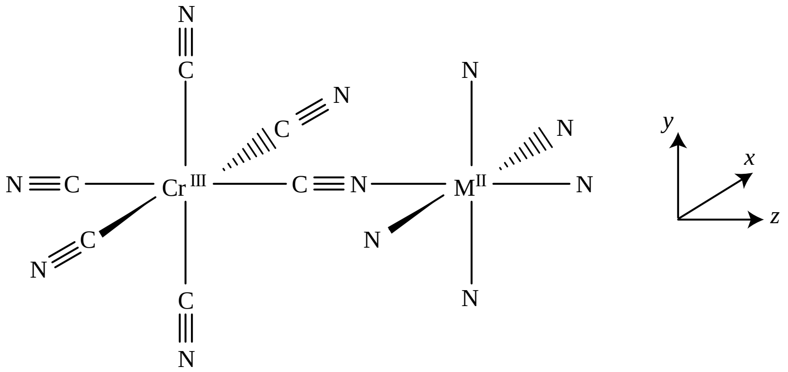
1. Introduction

The design of new systems with expected dimensionality and architecture is one of the challenges in molecular magnetism. Magnetic properties are intimately related to dimensionality. Extended systems possessing three-dimensional structure are expected to order magnetically below a critical temperature T_c. Polynuclear molecules with a high-spin ground state and large magnetic anisotropy may behave as nanomagnets.

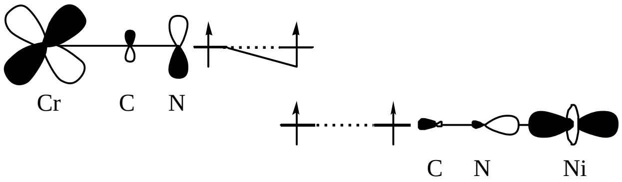
We have been involved during the last few years in the design of molecular systems where dimensionality and, thus, magnetic properties may be addressed chemically by means of organic chelating ligands. In this paper, we will focus on the synthesis of cyanide-bridged systems obtained from the reaction of hexacyanochromate(III) and mononuclear complexes of general formula $[M^{II}L_n(H_2O)_{6-n}]^{2+}$, where M may be Ni or Mn, and L_n is a chelating ligand that blocks two, four or five of the coordination sites around the metal. Depending on the nature of the chelating ligand—(i) the number of chelating sites, (ii) the size of the ligand, (iii) the isomer used for a given number of chelating sites (for tetradentate ligands cis and trans isomers)—an infinite number of possibilities can be expected and making prediction is hazardous. Our endeavour is directed towards the study of different parameters that influence the dimensionality and the architecture for a given dimension in order to establish some rules that enable a control of the properties of the final material.

In this paper, we present the crystallographic structures and the magnetic properties of a series of Cr^{III}–M^{II} cyanide-bridged compounds; our aim is to present our work more from the chemical design point of view, without going deeply into the subtleties of the magnetic properties. The paper is organized as follows: § 2 is an introduction to the nature of the exchange interaction through the cyanide bridge

Phil. Trans. R. Soc. Lond. A (1999) **357**, 3139–3158



Scheme 1.



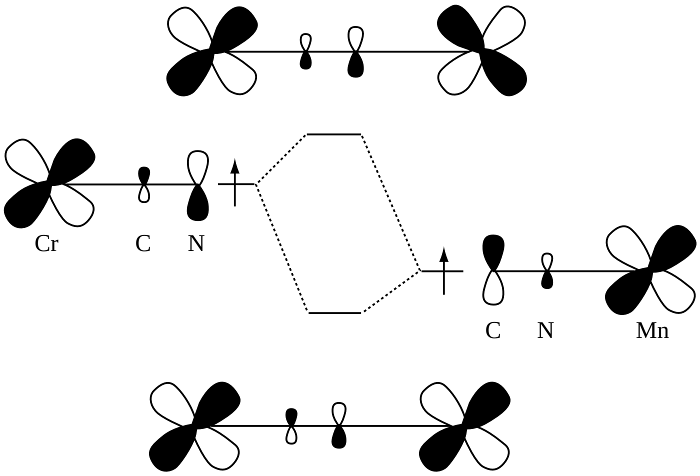
Scheme 2.

between Cr^{III} and Ni^{II} on one hand and Cr^{III} and Mn^{II} on the other hand. A description of the structure and the magnetic properties of several compounds according to the nature of the organic ligand L_n can be found in § 3, and a brief discussion mainly centred on the possibilities of predicting the dimensionality and the architecture of new cyanide-bridged materials is included in this section. A general conclusion is given in § 4.

2. Short-range exchange interaction through the cyanide bridge

Let us consider the molecular fragment depicted in scheme 1, in which the local symmetry around each metal ion is octahedral.

When M is Ni, the three single electrons of Cr^{III} are described by t_{2g} orbitals strictly orthogonal to the e_g orbitals of the two Ni^{II} single electrons. This is shown in scheme 2 between the Cr^{III} d_{yz} and the Ni^{II} d_{z^2} orbitals. Ginsberg (1971) was the first to predict that ferromagnetic interaction is expected from the interaction between Cr^{III} and Ni^{II} ions through a linear bridge. We find, experimentally, that the exchange coupling interaction between Cr^{III} and Ni^{II} through the cyanide bridge is, indeed, ferromagnetic in nature. Kahn (1985) showed that the amplitude of the ferromagnetic interaction depends on the overlap density defined as $\rho(1) = a(1)b(1)/r_{12}$. When the bridge is a single atom, the overlap density concentrated on a very small region of space between the two metal ions is expected to have a large local value, leading to an appreciable ferromagnetic exchange interaction. In Cr^{III}–Ni^{II} cyanide-bridged systems, the metal–metal distance is *ca.* 5.2 Å, the overlap density is expected to be spread over the carbon and nitrogen atoms leading to a small amplitude for the interaction. Gadet *et al.* (1992) have shown, using semi-empirical calculations, that this was not the case, because despite the presence of a two-atom bridge, the overlap



Scheme 3.

density is mainly localized on the nitrogen atom, giving a large local value for the overlap density. Scheme 2 shows that the contribution of the nitrogen atom to the $\mathrm{Cr^{III}}$ d_{yz} and the $\mathrm{Ni^{II}}$ d_{z^2} magnetic orbitals is larger than that of carbon.

When M is Mn the situation is different, since $\mathrm{Mn^{II}}$ has five single electrons: three on $\mathrm{t_{2g}}$ orbitals and two on $\mathrm{e_g}$ orbitals. The overall exchange coupling constant J can be expressed as

$$J_{\mathrm{CrMn}} = \frac{1}{n_{\mathrm{Cr}} n_{\mathrm{Mn}}} \sum j_{\mu\nu}, \tag{2.1}$$

where n is the number of single electrons for a given metal ion and $j_{\mu\nu}$ are the different exchange pathways between pairs of magnetic orbitals. Fifteen pathways are possible, corresponding to $n_{\mathrm{Cr}} n_{\mathrm{Mn}} = 15$, but only a few are effective. Effective pathways that contribute to the interaction are those corresponding to magnetic orbitals possessing a contribution to the cyanide bridge between the metal ions. Of the possible 15 pathways, only four should be taken into account, i.e. j_{xz-xz}, j_{yz-yz}, j_{xz-xz}, j_{xz-z^2} and j_{yz-z^2}. The former two pathways are built from orbitals with non-zero overlap integral (scheme 3), while the latter correspond to orthogonal orbitals, as in the case of $\mathrm{Ni^{II}}$.

For $\mathrm{Cr^{III}Mn^{II}}$ cyanide-bridged compounds, the interaction will be the result of two contributions: one antiferromagnetic, due to the overlap between $\mathrm{Cr^{III}}$ and $\mathrm{Mn^{II}}$ $\mathrm{t_{2g}}$ magnetic orbitals; and the other ferromagnetic, due to $\mathrm{t_{2g}}$–$\mathrm{e_g}$ orthogonal orbitals. In such a case, the overall interaction depends on the nature of the dominant interaction. Experimental results presented below clearly show that the antiferromagnetic contribution dominates and that the interaction between $\mathrm{Cr^{III}}$ and $\mathrm{Mn^{II}}$ through cyanide is antiferromagnetic. Our prediction is based on the assumption that the Cr–C–N–M sequences are linear. This is the case in most of the compounds, but if the CNM angle deviates from linearity by more than 10°, it is possible to observe a Fe(III)–Ni(II) antiferromagnetic interaction, as was postulated by El Fallah *et al.* (1996) to explain the ferrimagnetic behaviour in $[\mathrm{Ni(tren)}]_3[\mathrm{Fe(CN)_6}]_2$.

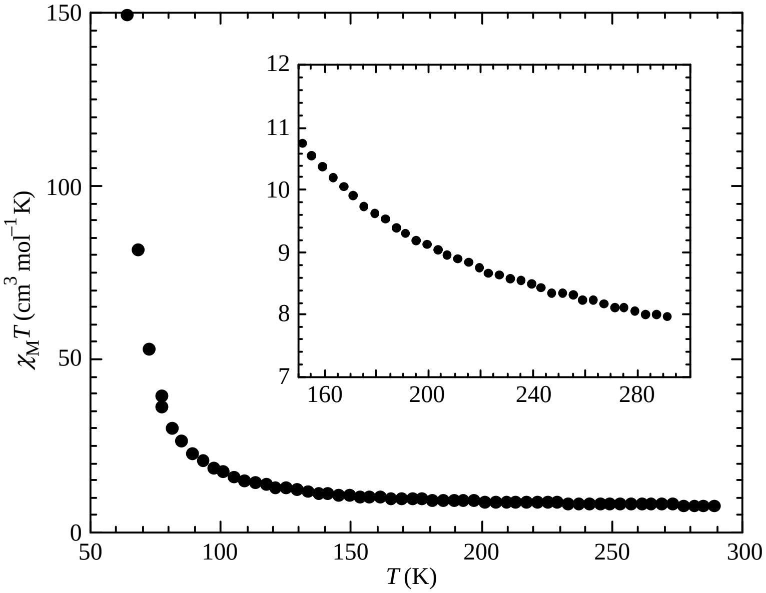


Figure 1. $\chi_M T = f(T)$ at $H = 100$ Oe for CrNien.

3. From three-dimensional systems to polynuclear complexes

(*a*) *Three-dimensional* $[Cr(CN)_6]_2[Ni(1,2\text{-diaminoethane})]_3 \cdot 2H_2O$: *a ferromagnet*

$[Cr(CN)_6]_2[Ni(1,2\text{-diaminoethane})]_3 \cdot 12H_2O$, referred to simply as CrNien below, is obtained by reacting $[Ni(1,2\text{-diaminoethane})(H_2O)_4]Cl_2$ with $K_3[Cr(CN)_6]{\cdot}2H_2O$ in water. A yellow precipitate appears immediately; it is filtered, thoroughly washed with water and dried under vacuum. The crystal structure is determined on a powder sample by refining the X-ray diffraction diagram using the Rietvelt method. The refinement is done using the $Fm3m$ space group of Prussian blue. The unit cell is face-centred cubic with a parameter a equal to 10.46 Å corresponding to the Cr^{III}–Cr^{III} distance. Each Cr atom is surrounded by six Ni atoms through the cyanide bridge, and each Ni is surrounded by only four Cr and one 1,2-diaminoethane bidentate ligand.

When decreasing temperature, the $\chi_M T$ product increases from a value that corresponds to non-interacting spins at room temperature (7.29 cm^3 mol^{-1} K) and diverges *ca.* $T = 60$ K (figure 1). The increase in $\chi_M T$ is the signature of a short-range ferromagnetic interaction between Cr^{III} and Ni^{II} through the cyanide bridge.

In order to study the behaviour at low temperature, magnetization versus temperature measurements were performed in three different regimes (figure 2). The starting temperature is $T = 70$ K and the field is set at 30 Oe, the temperature is decreased down to 3 K, which affords the field cooled magnetization (FCM). At $T = 3$ K, the field is cut-down and the magnetization measured with increasing temperature up to $T = 70$ K, which gives the remnant magnetization (REM) curve that goes to zero at $T = 40$ K. The zero-field cooled magnetization (ZFCM) curve is obtained by cooling the sample in zero field down to $T = 3$ K; the field is set again at 30 Oe and the magnetization measured from 3 K to 70 K. These three curves are indicative of a three-dimensional magnetic order, and since the short-range interaction is

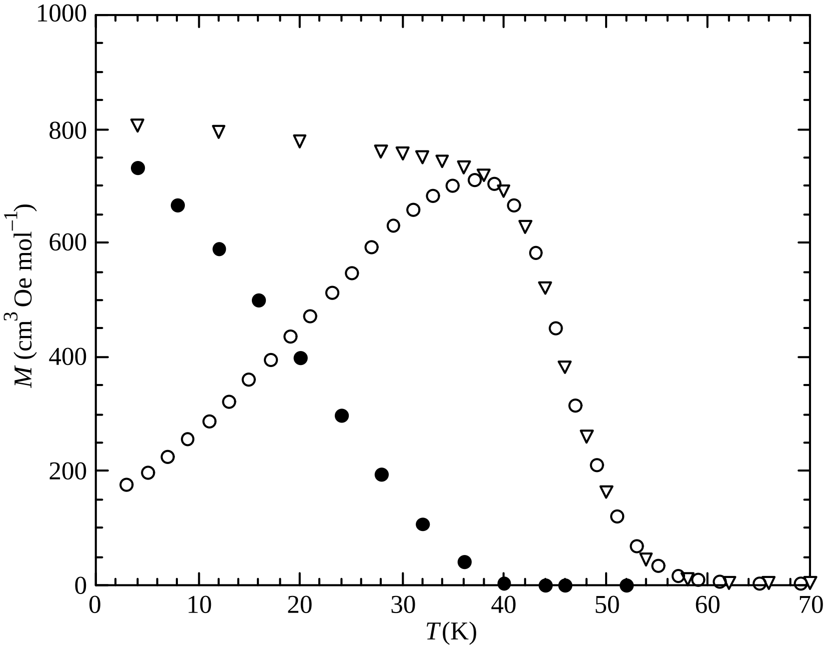


Figure 2. (▽) FCM, (●) REM and (○) ZFCM curves for CrNien.

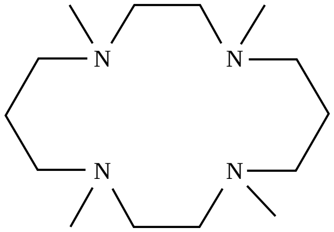
ferromagnetic in nature, the order is a ferromagnetic one. The ordering temperature T_c is defined as the temperature where the REM curve goes to zero, which should correspond to the temperature where the FCM and the ZFCM curves merge. For CrNien, T_c is equal to 40 K.

The cubic structure of CrNien allows us to use the molecular-field approach to estimate the value of the exchange coupling constant J_{CrNi} between $\mathrm{Cr^{III}}$ and $\mathrm{Ni^{II}}$. The relationship between T_c and J_{CrNi} is given by (Ferlay 1999)

$$T_c = \frac{2}{k} y\sqrt{y}|J_{\mathrm{CrNi}}|\sqrt{S_{\mathrm{Cr}}(S_{\mathrm{Cr}}+1)S_{\mathrm{Ni}}(S_{\mathrm{Ni}}+1)}, \tag{3.1}$$

where k is the Boltzmann constant, S_{Cr} $(= 3/2)$ and S_{Ni} $(= 1)$ are the $\mathrm{Cr^{III}}$ and $\mathrm{Ni^{II}}$ spins, respectively, and y is the chromium-to-nickel atomic ratio (2/3) within the compound. Applying equation (3.1) with $T_c = 40$ K leads to a value of $9.3\ \mathrm{cm^{-1}}$ for the exchange coupling constant J_{CrNi}.

The introduction of the bidentate ligand in the coordination sphere of $\mathrm{Ni^{II}}$ does not alter the overall structure, which is still the same as Prussian blue, this is because the ligand used is not bulky enough to destroy the cubic arrangement. We have increased the size of the bidentate ligand by substituting the four hydrogen atoms on the amine groups by four methyl groups in the mononuclear $\mathrm{Ni^{II}}$ precursor; this leads to the formation of a new system possessing a non-cubic structure, as was shown from the powder diffraction pattern. Unfortunately, no single crystals were obtained, and, hence, an analysis of the new structure could not be undertaken.



Scheme 4.

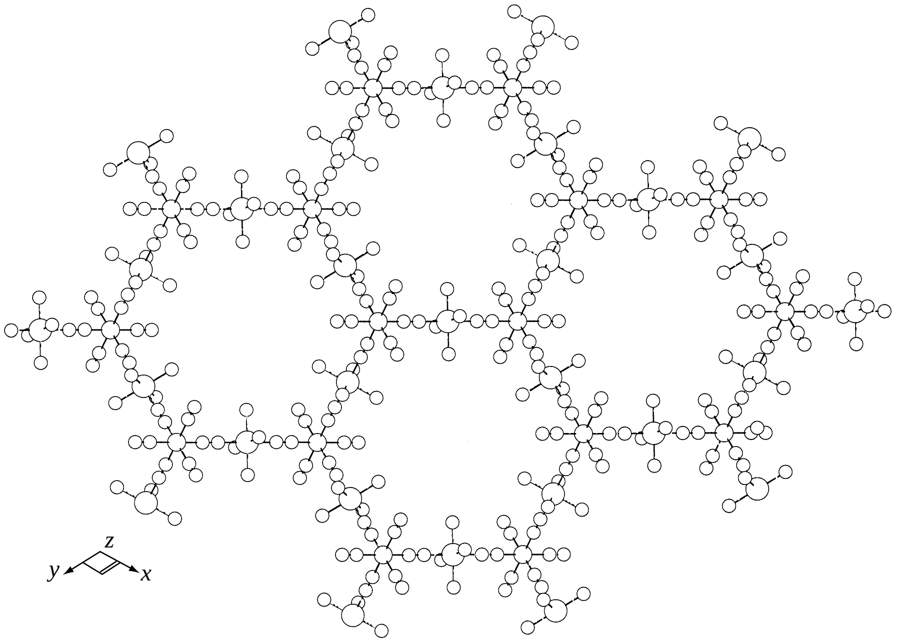


Figure 3. View perpendicular to the layer (along the *c*-axis) for CrNitmc; the tmc's carbon atoms were removed for clarity.

(*b*) *Two-dimensional* $[\mathrm{Cr(CN)_6}]_2[\mathrm{Ni(tmc)}]_3 \cdot 12\mathrm{H_2O}$: *a metamagnet*

(i) *Description and discussion of the structure*

When the mononuclear complex $[\mathrm{Ni^{II}(tmc)}](\mathrm{ClO_4})_2$, where tmc is a tetradentate ligand (scheme 4), is reacted with hexacyanochromate(III) in water or in acetonitrile, a neutral 3/2 stoichiometric compound of formula $[\mathrm{Cr(CN)_6}]_2[\mathrm{Ni(tmc)}]_3 \cdot 12\mathrm{H_2O}$ (referred to simply as CrNitmc below) is obtained independently of the relative stoichiometry of the reactants.

X-ray diffraction on single crystals reveals a structure built up from corrugated layers, as shown in figures 3 and 4. The layers are stacked along the *c*-axis (figure 5), the interlayer metal–metal distance is 9.25 Å. The 12 water molecules in the interlayer space are disordered.

The Cr–C distances for the three bridging cyanides (2.059(11) Å) are slightly shorter than those of non-bridging ones (2.098(11) Å). The Ni surrounding is more

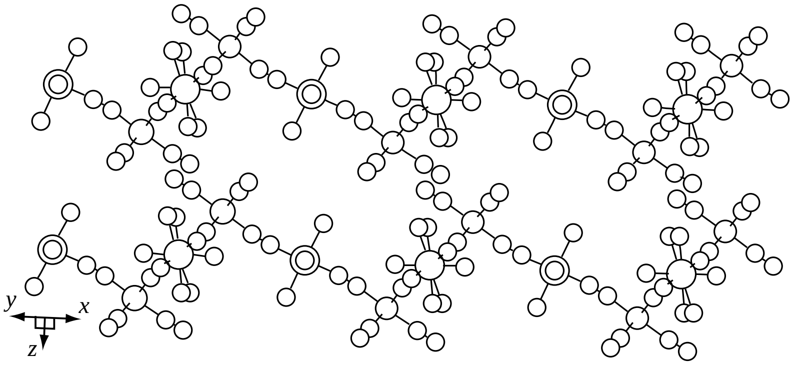


Figure 4. View (two layers) perpendicular to the *c*-axis for CrNitmc.

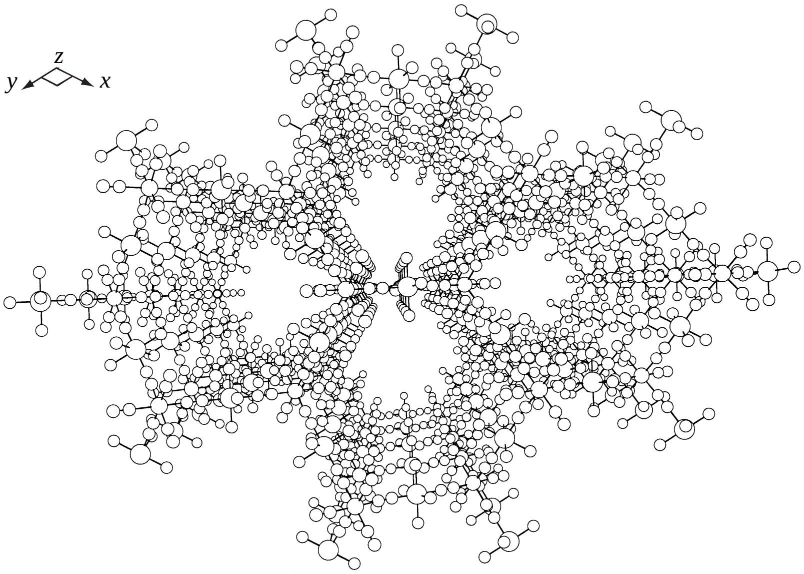


Figure 5. Perspective view along the *c*-axis for CrNitmc.

distorted: within the tmc plane, the Ni–N distances have a difference of *ca.* 0.1 Å (Ni–N(1) = 2.24(2) Å, Ni–N(4) = 2.313(15) Å). The Ni–N axial distances are much shorter (Ni–N(10) = 2.086(11) Å) (figure 6). The local Ni^{II} environment may then be considered as a compressed octahedron along the Cr–CN–Ni–NC–Cr connection perpendicular to the tmc plane.

Each $Cr(CN)_6$ unit is surrounded in a facial manner by three Ni(tmc) complexes; the Ni(tmc) units bridge two $Cr(CN)_6$ in a *trans* fashion. The arrangement of the $Cr(CN)_6$ moieties around the Ni was expected because $[Ni(tmc)]^{2+}$ has its two available sites in the *trans* position. The number of Ni atoms around Cr is dictated by the neutrality of the compound, which imposes a Ni/Cr:3/2 stoichiometry. Let us analyse the possible structures that may grow by considering different starting local arrangements around the metal ions. Before doing that we assume that

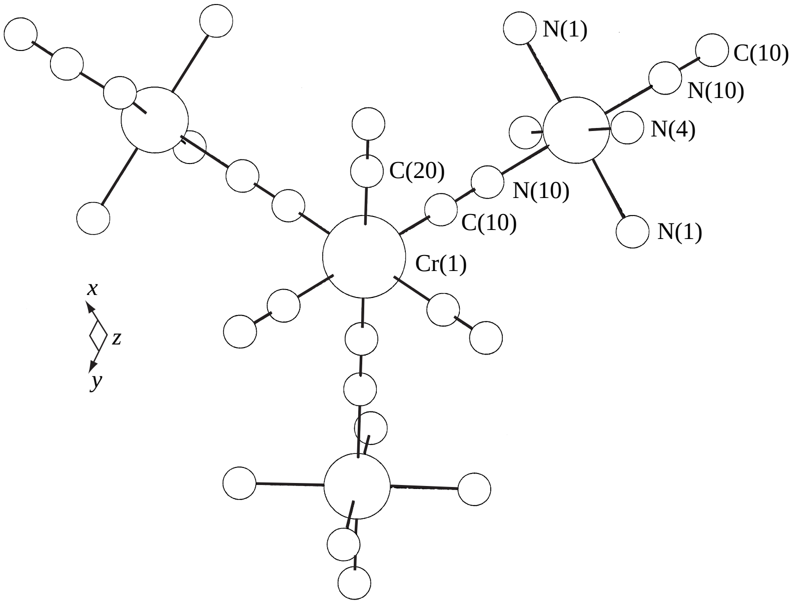
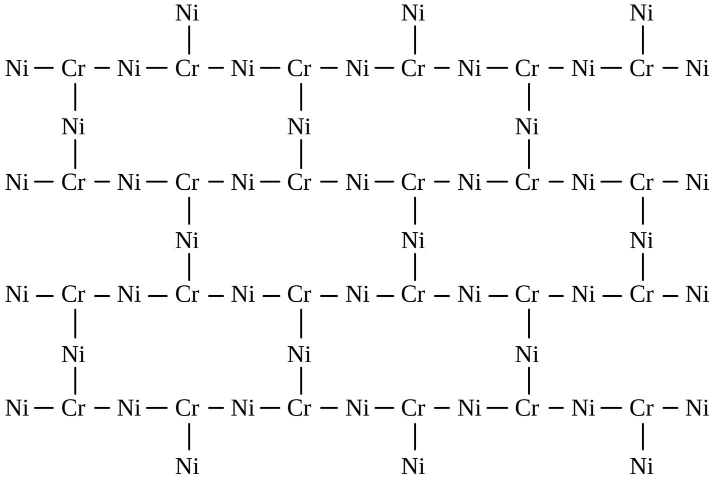
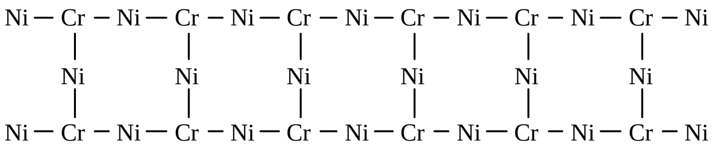


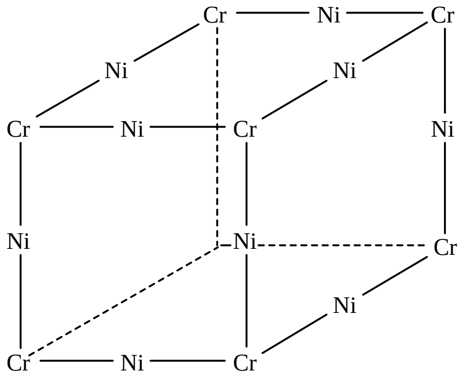
Figure 6. View of a $CrNi_3$ unit along the C_3 axis of the $Cr(CN)_6$ complex for CrNitmc.



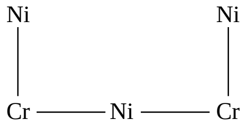
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

(i) the nature of tmc imposes a *trans* arrangement of two $Cr(CN)_6$ units around each Ni^{II} ion; and

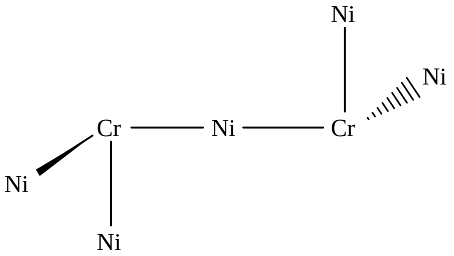
(ii) the neutrality of the compound allows each Cr to be surrounded by three Ni: meridional and facial spatial $CrNi_3$ arrangements will then be considered.

A meridional $CrNi_3$ arrangement leads either to a bidimensional flat layer or a double chain stair-like structure (schemes 5 and 6).

For the facial arrangement, one expects the formation of a discrete cube-like molecule (scheme 7) or a bidimensional corrugated layered compound. Experiment shows that the latter possibility has been obtained. One may think that within the powder there is a mixture of different compounds; this hypothesis is ruled out because the magnetic behaviour of a powder sample obtained by rapid precipitation in water and that of a powder sample obtained by grinding a collection of single crystals is identical.

It is not easy to rationalize the selectivity of the reaction that leads to the observed structure (the reaction gives *ca.* 80% yield of powder when performed in water), especially because the cube-like discrete molecule arrangement should, on an entropy basis, be thermodynamically favoured. The entropy contribution to the total free energy favours the formation of a compound built up from discrete entities, rather than a polymeric one. It is possible, however, to invoke one argument in favour of the corrugated layer structure. A common spatial arrangement found in the three theoretical structures is shown in scheme 8.

This arrangement of the five complexes in the same plane (two $Cr(CN)_6$ and three Ni(tmc)) imposes a steric hindrance between the three tmc ligands. In order to preclude hindrance between the organic ligands, the compound locally adopts the only other arrangement (scheme 9) that, when translated in two dimensions, leads to the observed structure.



Scheme 9.

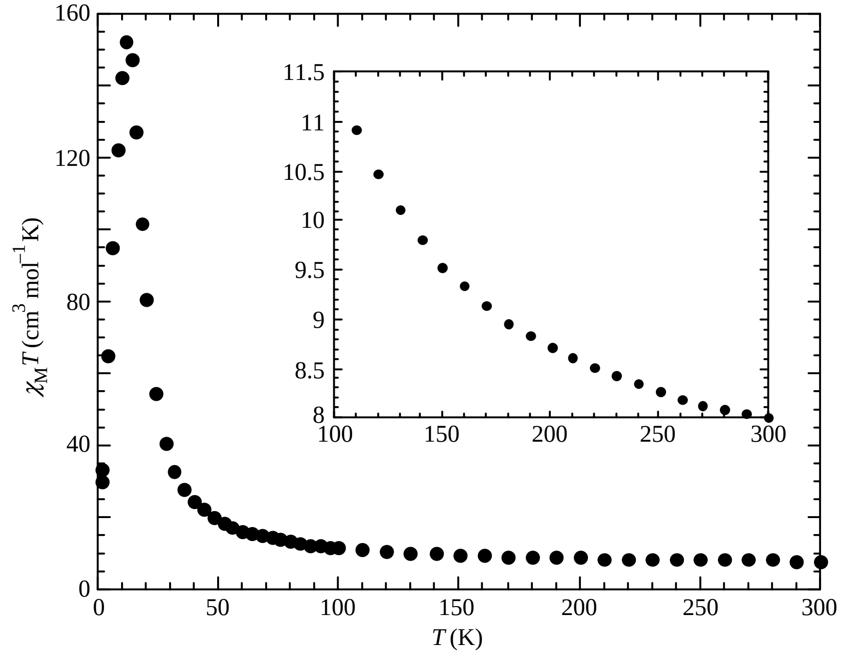


Figure 7. $\chi_{\mathrm{M}}T = f(T)$ at $H = 1000$ Oe for CrNitmc.

(ii) *Magnetic properties*

The behaviour of the $\chi_{\mathrm{M}}T = f(T)$ curve (figure 7) between room temperature and $T = 2$ K is similar to that of the preceding compound. As expected, the short-range interaction between $\mathrm{Ni^{II}}$ and $\mathrm{Cr^{III}}$ through the cyanide bridge is ferromagnetic within the bidimensional layer. The maximum in the curve corresponds to a $\chi_{\mathrm{M}}T$ value of 155 cm^3 mol^{-1} K and occurs at $T = 12$ K. The corresponding spin value S is about 17. This is a rough measure of the number of correlated spins within the plane; it corresponds to nine $\mathrm{Ni^{II}}$ and six $\mathrm{Cr^{III}}$ ions having their spins in the same direction.

In order to get insight into the compound properties at low temperature, a powder sample was blocked with parafilm in order to preclude particle motion at low temperature, and the magnetization was measured between 50 and 2 K in an applied field of 30 Oe (figure 8). Below 20 K, the magnetization rises abruptly, attains a maximum of 523 cm^3 Oe mol^{-1} at $T = 14$ K, decreases and then levels off at 5 K with a value

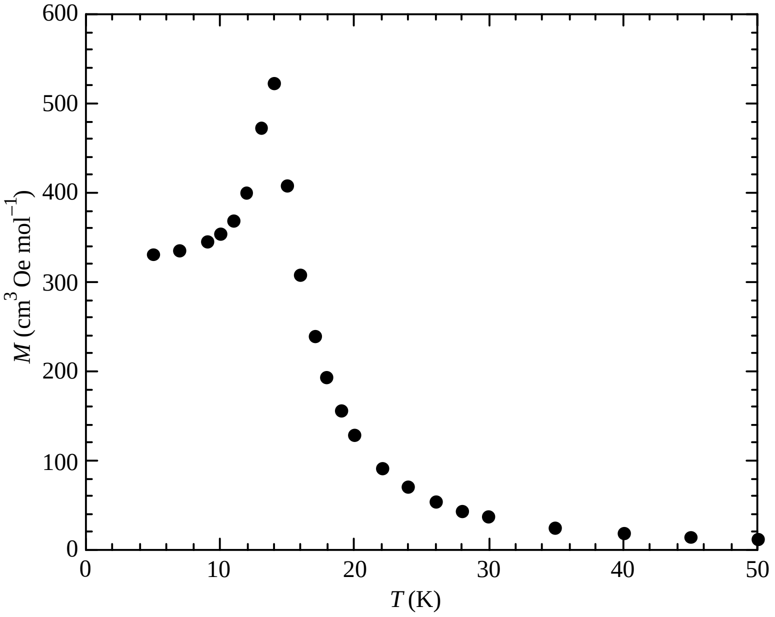


Figure 8. $M = f(T)$ at $H = 30$ Oe for CrNitmc.

of 332 cm^3 Oe mol^{-1}. The presence of a maximum in the FCM curve indicates the presence of an antiferromagnetic three-dimensional order between the ferromagnetic planes. At low temperature, the magnetization does not go to zero but to a value that corresponds to about two-thirds of the one observed at $T = 14$ K. This is the expected behaviour of an antiferromagnet with non-negligible anisotropy, as shown by de Jongh & Miedema (1974). In such compounds, if the magnetization is measured on a single crystal with the applied field parallel to the easy axis, the magnetization falls to zero at the ordering temperature T_{N}. When the field is perpendicular to the easy axis, the magnetization saturates at T_{N}. For a powder, the magnetization below T_{N} should, thus, correspond to the mean of the perpendicular and the parallel magnetization, $(2M_{\perp} + M_{\|})/3$, which is what we observe experimentally.

Layered antiferromagnets with non-negligible magnetic anisotropy are expected to behave in a different manner from antiferromagnets with extremely small anisotropy. Below T_{N}, the magnetization can be reversed abruptly when a magnetic field is applied, providing that the interlayer antiferromagnetic coupling responsible for the bulk behaviour is of the same order of magnitude as the applied magnetic field. Figure 9 shows that, at $T = 2$ K, it is possible to reverse the magnetization by applying a field of *ca.* 1200 Oe and to reach saturation with only 2000 Oe. The compound behaves as a metamagnet with a critical field H_{C} of 1200 Oe at $T = 2$ K. The magnetization at saturation is equal to $11.5\mu_{\mathrm{B}}$; this is the expected value for the paramagnetic aligned phase (or the field induced ferromagnetic phase) that corresponds to the sum of the spins of three Ni$^{\mathrm{II}}$ and two Cr$^{\mathrm{III}}$ metal ions $(M/N\beta = gS = 2 \times (3 \times 1 + 2 \times 3/2) = 12)$. The interlayer antiferromagnetic interaction is probably due to water molecules, which may link two different layers by hydrogen bonds between the nitrogen atoms of non-bridging cyanide groups. Van Langenberg *et al.* (1997) have shown that ferromagnetic three-dimensional order

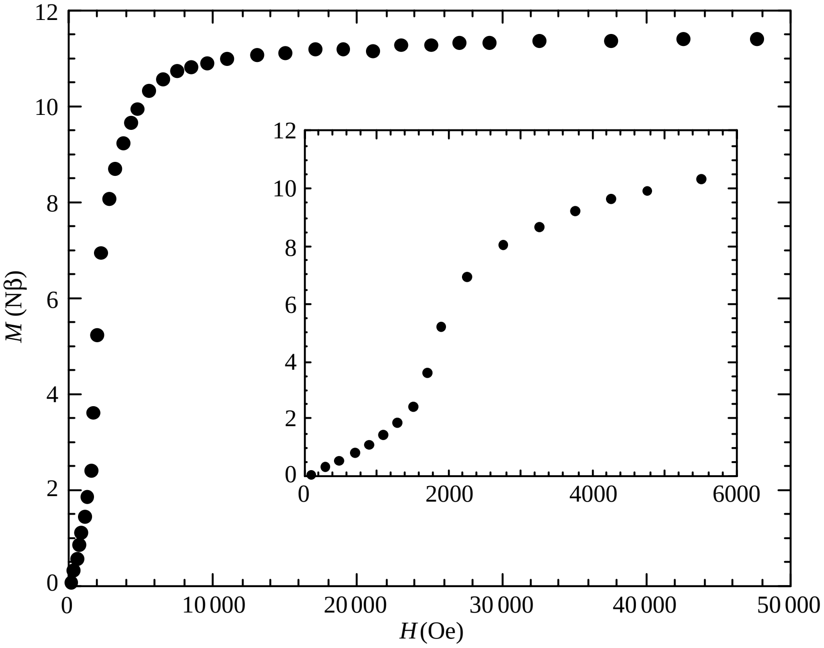
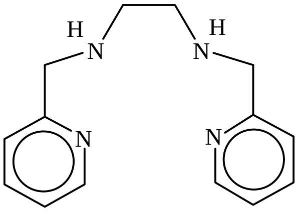


Figure 9. $M = f(H)$ at $T = 2$ K for CrNitmc.



Scheme 10.

occurs because of the presence of a three-dimensional hydrogen-bond network in $[Fe(CN)_6]_3[Ni(bpm)_2]_2 \cdot H_2O$. Unfortunately, the water molecules occupying the interlayer space are disordered; it is not possible to visualize the bond network responsible for the interaction between the layers.

(*c*) *One-dimensional* $[Mn(bispicen)]_3[Cr(CN)_6]_2 \cdot 6H_2O$

The reaction of *cis*$[Mn(bispicen)Cl_2]$, where bispicen is a tetradentate ligand (see scheme 10), with $((C_4H_9)_4N)_3[Cr(CN)_6]$ in methanol affords a yellow powder. Elemental analysis fits with the general formula $[Mn(bispicen)]_3[Cr(CN)_6]_2 \cdot 6H_2O$, referred to below as CrMnbispic.

Yellow block-shaped single crystals are obtained by letting two methanolic solutions of the two reactants diffuse for two months in an H-tube. The structure shows the formation of a one-dimensional system (figures 10 and 11). Two kinds of $Cr(CN)_6$ molecules are present: within the body of the chain one chromicyanide is surrounded by five Mn(bispicen) molecules: four in equatorial positions and one in an apical position leaving one non-bridging cyanide group; the second $Cr(CN)_6$ molecule is

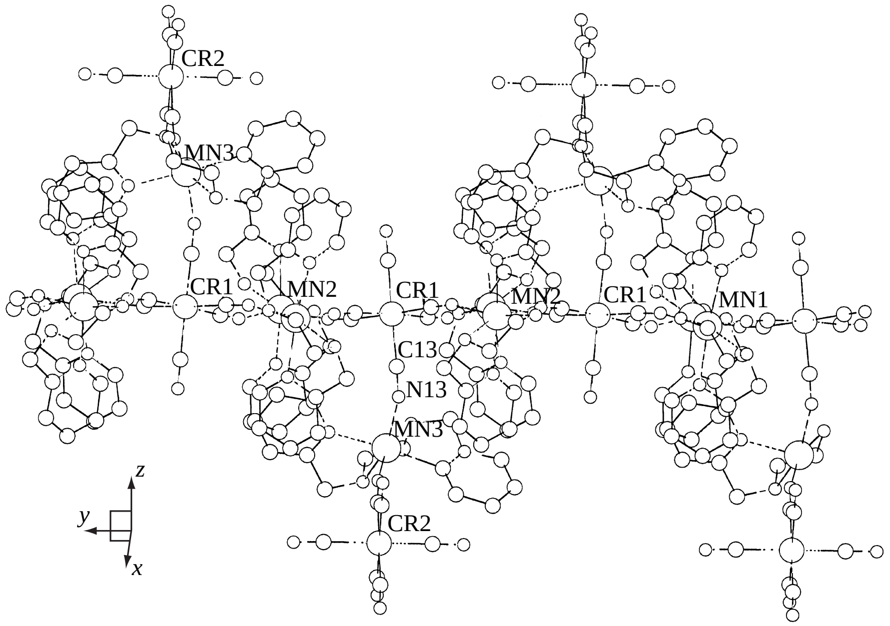


Figure 10. View of the architecture of one chain of CrMnbispic along the chain axis.

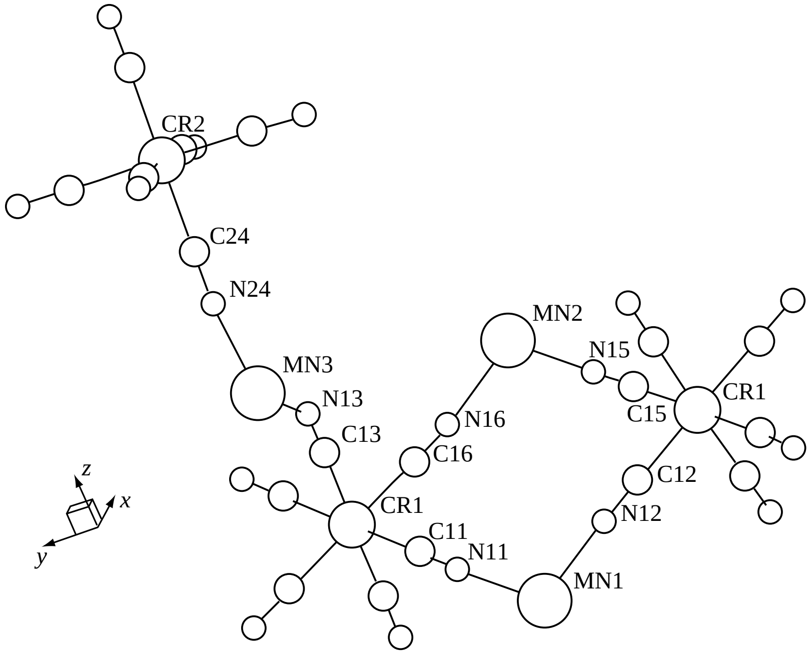
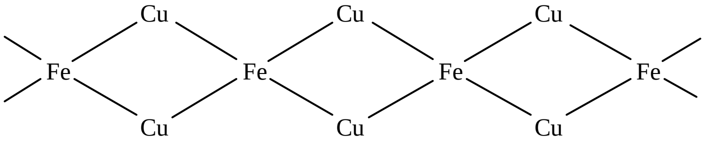


Figure 11. View of a hexanuclear fragment of CrMnbispic.



Scheme 11.

not bridging, it is linked only to the apical Mn unit. Each of the equatorial manganese molecules bridges two $Cr(CN)_6$ within the chain, and the apical manganese molecule bridges two $Cr(CN)_6$, one inside the chain and one outside.

The architecture of the body of the one-dimensional chain was observed, for the first time, by Morpugo *et al.* (1980) in $[Fe(CN)_6]_2[Cu(dien)]_3$. This compound is made from the association, within the same crystal, of a one-dimensional anionic chain $[Fe(CN)_6][Cu(dien)]_2^-$ with the same structure as the body structure of our compound and a cationic dimer $[Fe(CN)_6][Cu(dien)]^+$. Scheme 11 is a view of the chain architecture, the tridentate ligand diethylenetriamine (dien) capping the Cu^{II} ions and the bridging cyanide groups were removed for clarity. The reason for such similarity is the nature of the complex linking the metallocyanides in the two compounds, i.e. possessing two potential available sites for cyanide nitrogen in the *cis* position. The difference between the two structures is that in Morpugo's compound the binuclear unit is not linked to the chain, while in CrMnbispic it occupies one apical position on each in-chain chromium atom in an alternating way.

The Cr–C distances are all *ca.* 2.05 Å and the Cr–C–N angles are very close to 180° (176° on average). The surrounding of the Mn^{II} ions is more distorted. The distances between Mn and the nitrogen atoms belonging to the tetradentate ligands vary between 2.27 and 2.34 Å, while the distances between the manganese ions and the cyanide's nitrogen atoms are slightly shorter, 2.17 Å. The Mn–N–C angles deviate well from linearity:

$$\begin{aligned} &\mathrm{Mn(1)–N(12)–C(12)} = 177.61^\circ; \quad &&\mathrm{Mn(1)–N(11)–C(11)} = 163.75^\circ;\\ &\mathrm{Mn(2)–N(15)–C(15)} = 168.32^\circ; \quad &&\mathrm{Mn(2)–N(16)–C(16)} = 161.43^\circ;\\ &\mathrm{Mn(3)–N(24)–C(24)} = 167.18^\circ; \quad &&\mathrm{Mn(2)–N(13)–C(13)} = 146.75^\circ. \end{aligned}$$

The smaller angle corresponds to a cyanide bridge between the apical Mn ion and the chromium ion belonging to the body of the chain.

We present here the preliminary magnetic properties. At room temperature, the $\chi_M T$ value ($13.9\,cm^3\,mol^{-1}\,K$) is lower than that corresponding to the three non-interacting Mn^{II} ($S = 5/2$) and two non-interacting Cr^{III} ($S = 3/2$) ions (which have a $\chi_M T$ value of $16.875\,cm^3\,mol^{-1}\,K$). On decreasing the temperature, $\chi_M T$ decreases to a minimum at $T = 84\,K$ and then increases, as shown in figure 12. This behaviour indicates the presence of a short-range antiferromagnetic interaction between the Cr^{III} and the Mn^{II} ions as expected. Below $T = 30\,K$, $\chi_M T$ increases abruptly to a value of $308\,cm^3\,mol^{-1}\,K$ and then decreases at low temperature, which suggests the onset of a three-dimensional magnetic ordering. Further studies are necessary in order to understand the magnetic behaviour at low temperature. Measurements will be made on single crystals as well in order to check the magnetic properties along the parallel and the perpendicular axes of the chain.

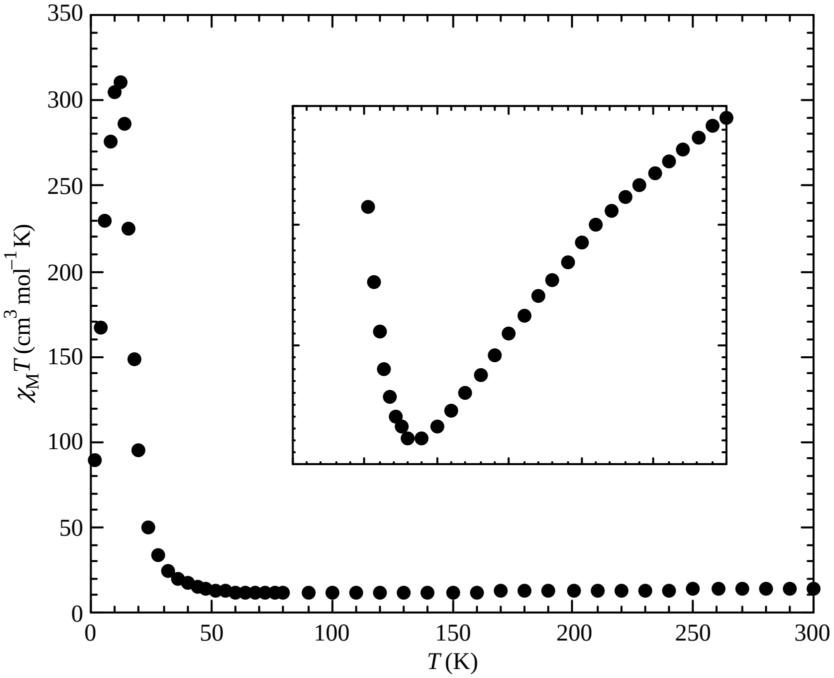
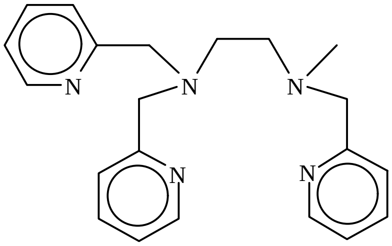
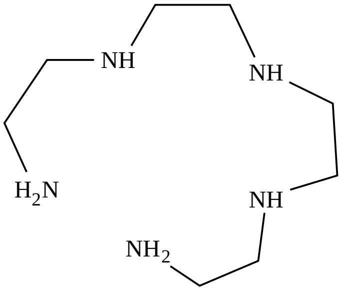


Figure 12. $\chi_M T = f(T)$ at $H = 1000$ Oe for CrMnbispic.



Scheme 12.



Scheme 13.

(*d*) *Zero-dimensional systems,* $\mathrm{CrMn_6}$ *and* $\mathrm{CrNi_6}$: *high-spin molecules*

In order to drastically reduce the dimensionality of the systems, it is possible to block all but one of the coordination sites on a metal ion (see Scuiller *et al*. 1996;

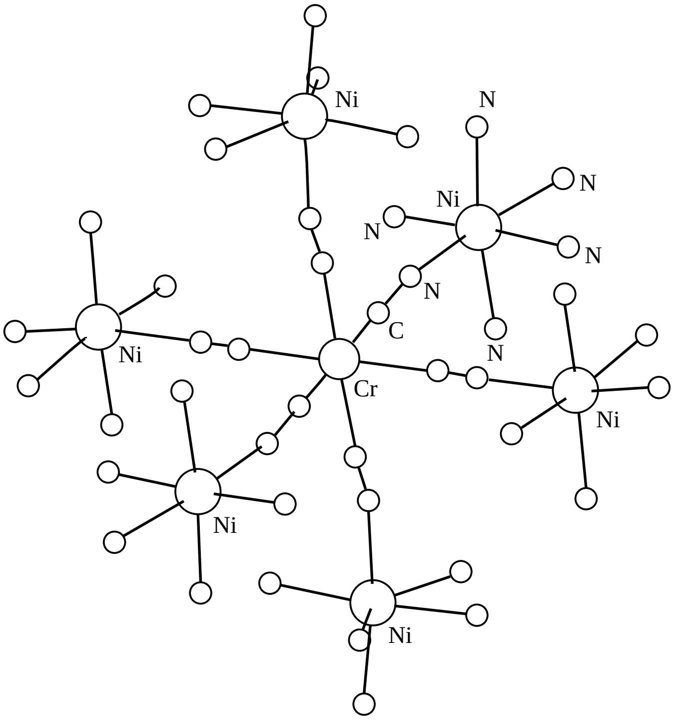


Figure 13. View of the heptanuclear molecule $CrNi_6$; the carbon skeleton of tetren is not shown here.

Mallah *et al.* 1995). Pentadentate ligands may be used to do this. We prepared two mononuclear complexes,

$$[Mn(trispicmeen)(H_2O)](ClO_4)_2 \quad \text{and} \quad [Ni(tetren)(H_2O)](ClO_4)_2,$$

where trispicmeen and tetren are depicted in schemes 12 and 13, respectively.

The synthesis of the heptanuclear compounds consists of adding a salt of chromicyanide to a solution containing an excess of the mononuclear compound. For

$$[Cr(CNMn(tripicmeen)_6](ClO_4)_9$$

(referred to simply as $CrMn_6$ below), the terabutylammonium salt and the acetonitrile solvent were used, the compound is isolated as powder by adding tetrahydrofuran to the mixture. $[Cr(CNNi(tetren)_6](ClO_4)_9$ ($CrNi_6$, see figure 13) is obtained by using the potassium salt in a 1/1 mixture of acetonitrile and water. Single crystals grow within a week if the mother solution is left to evaporate.

The $\chi_M T = f(T)$ plot for $CrMn_6$ (figure 14) presents a minimum $T = 210$ K, while that of $CrNi_6$ increases on cooling down and reaches, at $T = 4$ K, a value ($32.4\ \mathrm{cm^3\ mol^{-1}\ K}$) corresponding to a spin $S = 15/2$. This indicates the occurrence of an antiferromagnetic interaction between the central Cr^{III} and the six peripheral Mn^{II} in $CrMn_6$ and a ferromagnetic interaction for $CrNi_6$. The experimental $\chi_M T = f(T)$ data can be fitted to the $\chi_M T$ theoretical expression derived from the

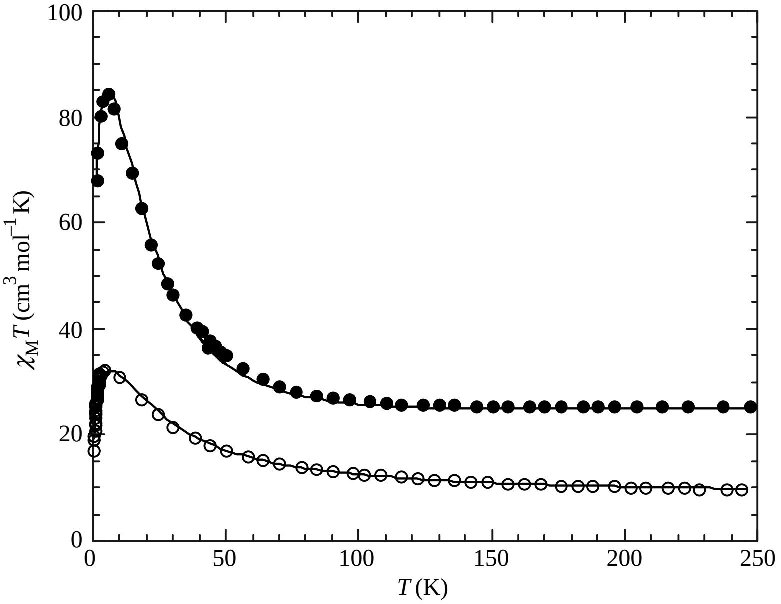


Figure 14. $\chi_M T = f(T)$ at $H = 100$ Oe for CrMn$_6$ (●) and for CrNi$_6$ (○). The lines correspond to the fit results.

following spin Hamiltonian:

$$H = -J_{\mathrm{CrM}} S_{\mathrm{Cr}} \sum_{i=1}^{6} S_{\mathrm{M}_i} + \beta g \left[\sum_{i=1}^{6} S_{\mathrm{M}_i} + S_{\mathrm{Cr}} \right] H + D S_z^2, \tag{3.2}$$

where J_{CrM} is the exchange coupling constant between Cr$^{\mathrm{III}}$ and M$^{\mathrm{II}}$, M is Mn or Ni, g is the g-factor, taken to be the same for the metal ions, S_{Cr} and S_{M} are Cr$^{\mathrm{III}}$ and M$^{\mathrm{II}}$ spin operators, and D is the zero-field splitting parameter. The fit gives the following results: for CrMn$_6$, $J_{\mathrm{CrMn}} = -8\,\mathrm{cm}^{-1}$, $g = 1.98$ and $D = 0.006\,\mathrm{cm}^{-1}$; for CrNi$_6$, $J_{\mathrm{CrNi}} = +15\,\mathrm{cm}^{-1}$, $g = 2.04$ and $D = 0.008\,\mathrm{cm}^{-1}$.

The magnetization versus field plots at $T = 2$ K confirm the nature of the ground state for the two compounds. Figure 15 shows that, for CrMn$_6$, saturation magnetization ($27\mu_{\mathrm{B}}$) corresponds to $S = 27/2$, where the six peripheral $S = 5/2$ spins are aligned in an anti-parallel fashion to the central $S = 3/2$ spin. For CrNi$_6$, the observed value of $15\mu_{\mathrm{B}}$ indicates that the $S = 15/2$ ground state is the result of parallel alignment of the local spins within the ground state.

The dynamic magnetic properties of CrNi$_6$ show the occurrence of a blocking of the $S = 15/2$ moment at $T_{\mathrm{B}} = 0.3$ K. Figure 16 shows the $\ln(\tau) = f(1/T)$ curve, where τ is the inverse of the frequency of the oscillating field in the AC susceptibility experiment, and T is the temperature of the maximum of the imaginary component of the susceptibility for a given frequency. The energy barrier corresponds to the slope of the $\ln(\tau) = f(1/T)$ curve and is found to be equal to $4\,\mathrm{cm}^{-1}$.

Assuming an axial anisotropy, the energy barrier is given by DS_z^2, where $S_z = 15/2$. It is possible to compute the value of the zero-field splitting parameter D to be $0.07\,\mathrm{cm}^{-1}$. This value is an order of magnitude more than the value extracted from fitting the $\chi_M T = f(T)$ data (see above). One reasonable explanation is that our

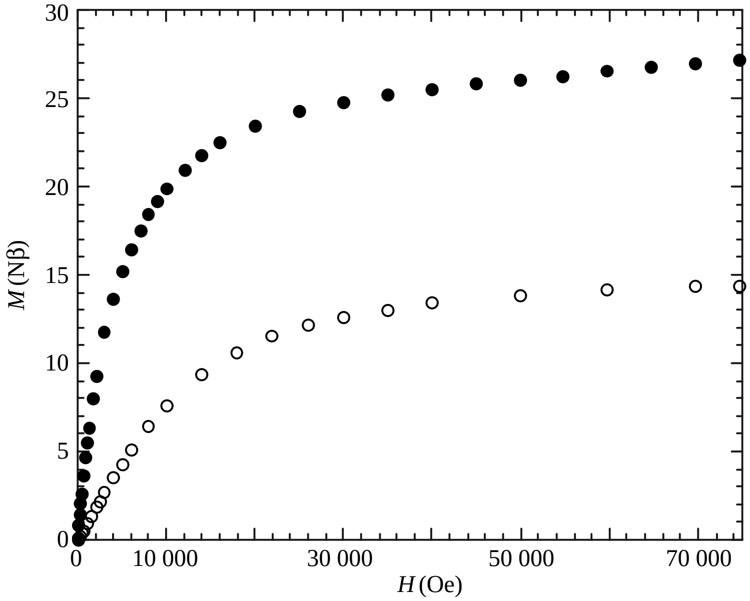


Figure 15. $M = f(H)$ at $T = 2$ K for $CrMn_6$ (●) and for $CrNi_6$ (○).

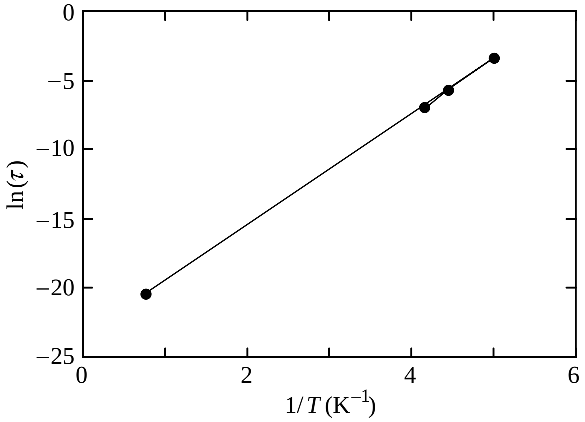


Figure 16. $\ln(t) = f(1/T)$ for $CrNi_6$: experimental data (●); and linear fit result (——).

assumption of an axial anisotropy as responsible for the blocking of the moment at low temperature is wrong, especially the notion that the $CrNi_6$ heptanuclear complex has an octahedral symmetry. However, the blocking of the magnetic moment is due to the presence of magnetic anisotropy, which is probably cubic in nature and not axial in this case.

4. Conclusion

We have shown how, everything being equal, the nature of the organic ligand can influence the dimensionality and, thus, the magnetic properties of cyanide-bridged systems. When one 1,2-diaminoethane, a bidentate ligand, is used as chelate for

Ni^{II}, the three-dimensional structure of Prussian blue analogues is not altered and a bulk magnetic order is observed. On the other hand, when pentadentate ligands are used as chelates, it is possible to preclude polymerization and stabilize heptanuclear high-spin molecules. The role of the organic ligand is clearly determinant. It is then possible to explore new systems possessing new architecture, such as the $[Mn(bispicen)]_3[Cr(CN)_6]_2 \cdot 6H_2O$ compound presented above. On the other hand, polynuclear complexes with very high-spin ground states may be designed as well. A nice example of a pentanuclear compound was reported by van Langenberg *et al.* (1997). This compound is obtained by using a Ni^{II} complex containing two bulky bidentate ligands, leaving two coordination sites available in the *cis* position. The bulkiness of the bidentate ligands precluded the formation of an extended network because of steric hindrance, and thus allowed the stabilization of a molecular complex. Another nice example is reported by Heinrich *et al.* (1998), who showed that substituting three cyanide ligands with a tridentate ligand leads to the formation of an octanuclear box-like molecule. In Long's compound, diamagnetic ions are used but similar cyanide-bridged compounds that contain 20 paramagnetic metal ions (scheme 7) may be designed providing a judicious choice of the chelating organic ligands.

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Discussion

P. Day (*The Royal Institution, London, UK*). Has Professor Mallah made a cluster containing a central ferrocyanide ion with six surrounding high-spin Fe(III)? Such a species would mimic the local structure of Prussian blue, for which we proposed a mechanism to explain the ferromagnetic exchange between Fe(III) involving the intervalence charge-transfer configuration many years ago (Mayoh & Day 1976).

T. Mallah. We have made a pentanuclear cluster containing a central ferrocyanide with four surrounding high-spin Fe(III) chelated by a pentadentate ligand containing two phenolato groups. The magnetic properties clearly show a ferromagnetic interaction between the high-spin Fe(III) ions through the diamagnetic low-spin Fe(II), as observed in Prussian blue. A mechanism involving the intervalence charge transfer configuration proposed by Mayoh & Day (1976) explains the ferromagnetic exchange interaction. Unfortunately, we were not able to observe the intervalence optical band in our compound because of the presence of an intense band centred at 580 nm due to the charge transfer between the phenolato groups and Fe(III).

Additional reference

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